

NOSC TD 1241



AD-A198 076

NOSC TD 1241

Technical Document 1241
February 1988

Laser Dye Synthesis — Group F Compounds

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San Diego State University Foundation
San Diego State University



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This report was prepared by the San Diego State University Foundation for Code 521 of the Naval Ocean Systems Center.

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			Approved for public release; distribution is unlimited.		
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S) NOSC TD 1241		
6a. NAME OF PERFORMING ORGANIZATION San Diego State University Foundation		6b. OFFICE SYMBOL (if applicable) SDSU	7a. NAME OF MONITORING ORGANIZATION Naval Ocean Systems Center		
6c. ADDRESS (City, State and ZIP Code) San Diego State University 5178 College Avenue San Diego, CA 92182		7b. ADDRESS (City, State and ZIP Code) San Diego, California 92152-5000			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable) ONR	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N66001-85-D-0203		
8c. ADDRESS (City, State and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO. 61153N	PROJECT NO. CH16	TASK NO. RR0130101	AGENCY ACCESSION NO. DN305 113
11. TITLE (Include Security Classification) Laser Dye Synthesis - Group F Compound					
12. PERSONAL AUTHOR(S) E. J. Grubbs					
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM Mar 1987 TO Jul 1987		14. DATE OF REPORT (Year, Month, Day) February 1988	
15. PAGE COUNT 11					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	auxochromic groups		
			laser dyes		
			coplanarity		
			deprotonation		
			bromination		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This report describes progress toward the syntheses of new potential laser dyes. It is anticipated that new substrates will allow upscaling of flashlamp-pumped dye lasers to higher energies. The criteria for assessment of these dyes include (a) the extent to which they show a lower laser action threshold, (b) their operational efficiencies, and (c) their photochemical stabilities compared with laser dyes previously evaluated. In principle, high optical quality and convenient cooling are obtainable using a flow system. Also, costs should be relatively small compared with those for solid-state lasers if reasonably short, high-yield synthetic routes can be found.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE PERSON T. Pavlopoulos			22b. TELEPHONE (Include Area Code) 619-553-2792		22c. OFFICE SYMBOL Code 521

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

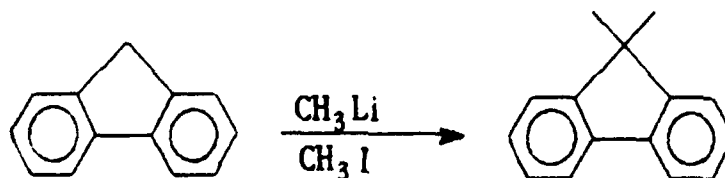
This report describes progress toward the syntheses of new potential laser dyes. It is anticipated that new substrates will allow upscaling of flashlamp-pumped dye lasers to higher energies. The criteria for assessment of these dyes include (a) the extent to which they show a lower laser action threshold, (b) their operational efficiencies, and (c) their photochemical stabilities compared with laser dyes previously evaluated. In principle, high optical quality and convenient cooling are obtainable using a flow system. Also, costs should be relatively small compared with those for solid state lasers if reasonably short, high yield synthetic routes can be found.

Pavlopoulos has proposed that improvements in presently available laser dyes may be realized by restricting chromophores and auxochromic groups to coplanarity or near coplanarity. The desired result of imposing these structural conditions is the reduction of intersystem crossing and thus improvements in quantum fluorescence yields. The targeted compounds described were designed to meet these objectives.

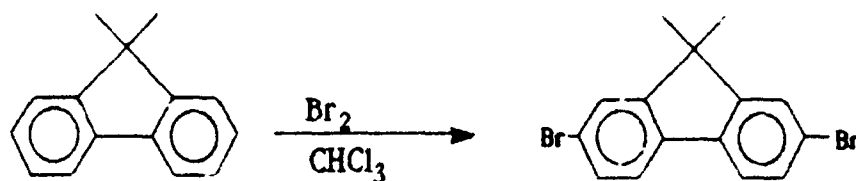
I. Derivatives of 9,9-Dimethylfluorene

An initial objective has been the functionalization of rotationally restricted biphenyls to facilitate the construction of a number of benzoxazoles, imidazopyridines, and extended stilbenes.

It has been found that under a variety of reaction conditions the C-9 hydrogens of fluorene are susceptible to either hydrogen atom abstraction or deprotonation. Thus, in order to block this reactive position, fluorene was dimethylated in 83% yield using the method of Bavin.¹ The dimethylated

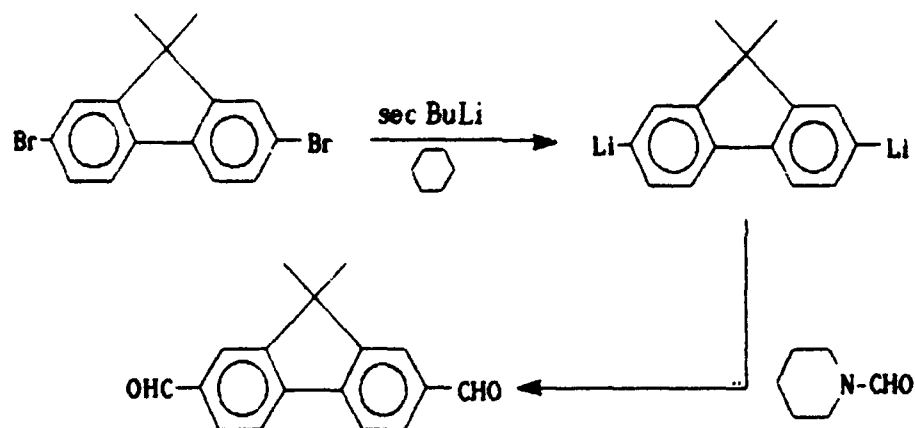


fluorene was then subjected to bromination using a procedure adapted from Hallas.² The 2,7-dibromo-9,9-dimethylfluorene was obtained in 64% yield following recrystallizations from ethanol. Dibromination is indicated by the

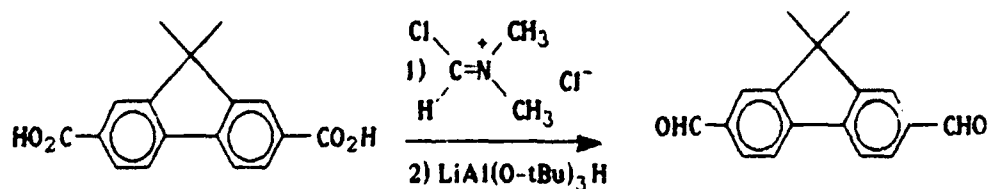


equal ^1H nmr integrals for the methyl (δ 2.3) and aromatic (δ 8.2) protons. The 2,7 bromine assignment is supported by simplicity of the ^{13}C nmr spectrum in which seven of the eight theoretically predicted absorptions are observed.³

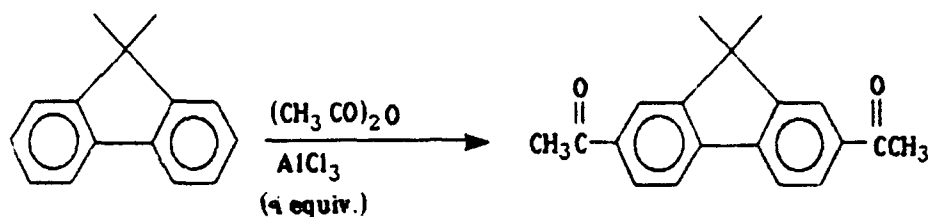
Conversion of the dibromodimethylfluorene to the corresponding dialdehyde was effected by metalation with *sec.* butyl lithium in cyclohexane followed by treatment with N-formylpiperidine. The ^1H NMR of the dialdehyde shows



the expected aldehyde absorption at δ 10.1 as well as aromatic and methyl proton signals with equal intensities. The mass spectrum shows the molecular ion at (m/z = 250). The dialdehyde was also prepared in lower yield by an alternate procedure⁴ starting with the diacid (the synthesis of which is described later in this report).

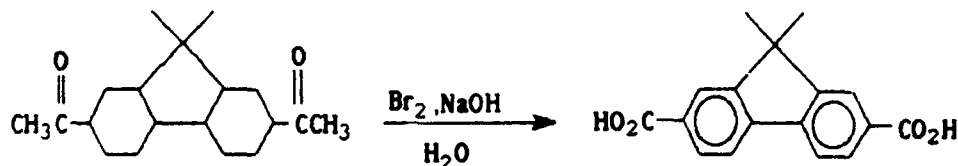


The 2,7-diacetyl derivative of 9,9-dimethylfluorene was prepared in 54% yield. This electrophilic substitution appears to be considerably less

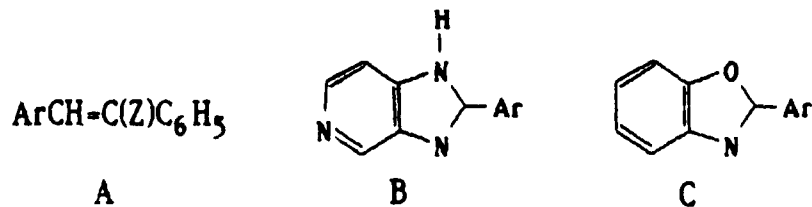


regioselective than the bromination. The 2,7-diacetyl derivative is accompanied by approximately 10% of a second isomer (most likely the 2,6 isomer) which is not easily separated. Monoacetylation of 9,9-dimethylfluorene was effected by use of 2 rather than 4 equivalents of aluminum chloride in the presence of an excess of acetic anhydride.

The conversion of diacetyl 9,9-dimethylfluorene to 9,9-dimethylfluorene 2,2-dicarboxylic acid (32% yield) was achieved using an aqueous solution of sodium hypobromite.

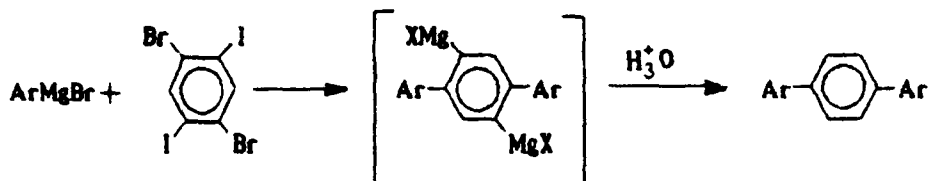


Studies are currently in progress directed towards conversions of the aldehyde and acid groups in these substrates to extended stilbenes (A), imidazopyridines (B) and benzoxazoles (C).

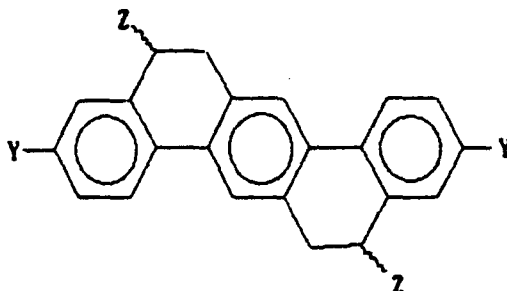


II. Synthetic approaches to Rotationally Restricted Terphenyls.

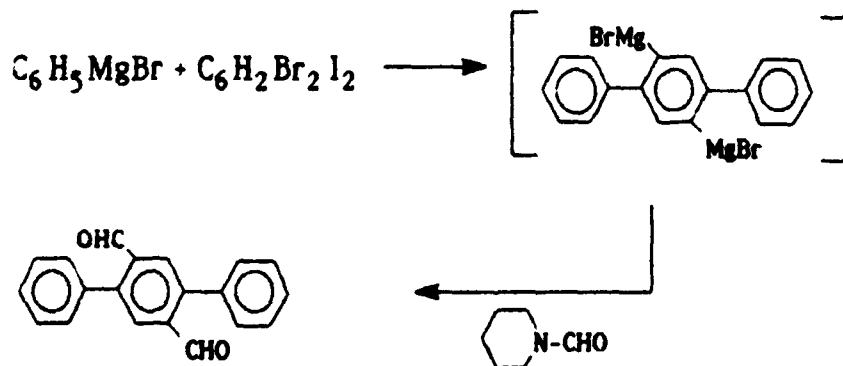
Hart⁵ has described a novel route to a variety of *p*-terphenyls involving the multistep reactions of aryl Grignard Reagents with 1,4-dibromo-2,5-iodobenzene. We have begun a study using this coupling strategy to prepare



precursors of tetrahydro 1,2-benzchrysene derivatives of the following type



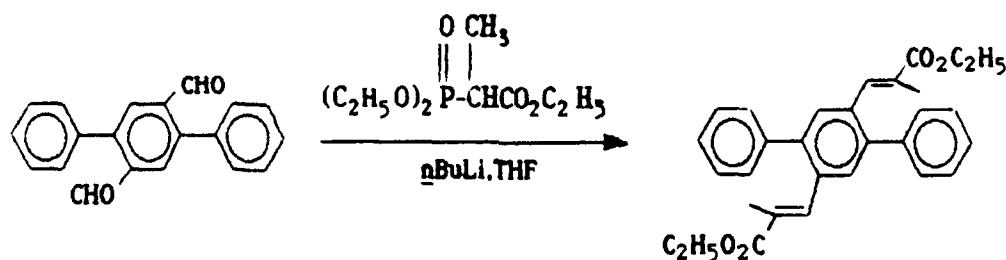
Our results can be summarized as follows. Phenylmagnesium bromide was allowed to react with dibromodiiodo benzene generating the assumed terphenyl di-Grignard intermediate which was then treated with N-formyl piperidine to generate the dialdehyde.



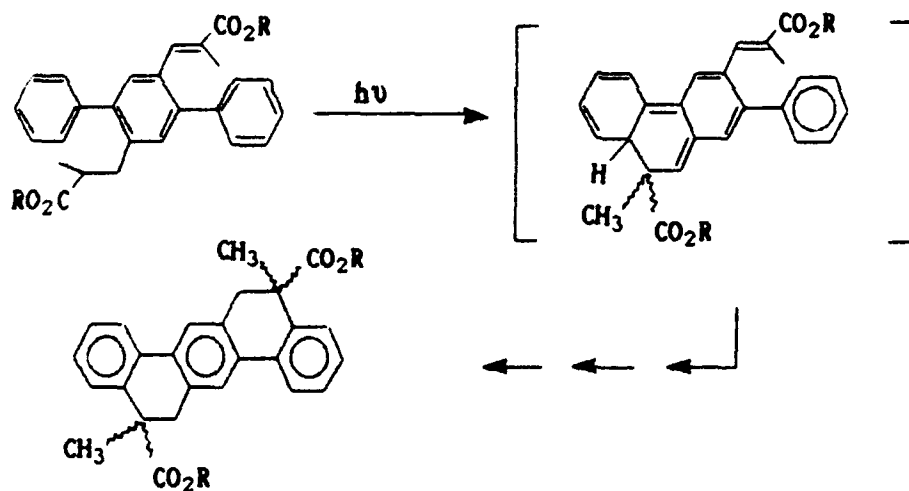
The dialdehyde was separated from unreacted starting materials and side products by a combination of chromatography and crystallization. The purified product was obtained in 19% yield. A major side product was identified as 2,5-dibromo-4-iodobenzaldehyde. The ^1H NMR spectrum of the dialdehyde shows the expected two-proton aldehyde resonance at δ 10.1 as well as a two-proton aromatic singlet at δ 8.1 attributable to the central ring

hydrogens, and a ten-proton multiplet at δ 7.5 resulting from the terminal rings. The mass spectrum reveals the molecular ion (also parent ion) at m/z - 286.

Reaction of the dialdehyde with triethylphosphonopropionate in the presence of *n*-butyl lithium generated the bis unsaturated ester in 66% yield.



The final step in this reaction sequence will be a double photocyclization followed by *in situ* 1,5-sigmatropic hydrogen shifts as shown:



Similar photochemical cyclizations of other phenylstyrene derivatives are well documented.⁶

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